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J.E. Reaugh

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COMPUTER SIMULATIONS TO STUDY THE HIGH-PRESSURE DEFLAGRATION OF HMX

John E. Reaugh

*HE and Organics Group, Physics and Applied Technologies, Lawrence Livermore National Laboratory,
Livermore CA 94551*

Abstract. The accepted micro-mechanical picture of the build-up of detonation in solid explosives from a shock is that imperfections are a source of hot spots. The hot spots ignite and link up in the reaction zone by high-pressure deflagration. Although the deflagration is subsonic, there are so many ignition sites that the pressure build-up is rapid enough to strengthen the initial shock. Quantitative advances in this research require a detailed understanding of deflagration at the high pressure, 1 to 50 GPa, which is present in the reaction zone. We performed direct numerical simulations of high-pressure deflagrations using a simplified global (3-reaction) chemical kinetics scheme. We used ALE-3D to calculate coupled chemical reactions, heat transfer, and hydrodynamic flow for finite-difference zones comprising a mixture of reactants and products at pressure and temperature equilibrium. The speed of isobaric deflagrations depends on the pressure and initial temperature. We show how this dependence changes with kinetic parameters, including the order of the last reaction step and the heat of formation of the species formed, relative to the reactant.

INTRODUCTION

Starting in the 1940's, explosives researchers became aware of the safety hazards that resulted from the presence of 0.1 to 10 μm gas bubbles or voids in solid and liquid explosives [1,2]. Such defects made the explosive more sensitive to shock. In the design of slurry explosives, defects are added to make the mixture detonable in the desired borehole diameter, but in solid and liquid explosives, they are reduced to minimize the sensitivity to handling accidents. In the reaction zone of a detonation, these voids become hot spots by their asymmetric collapse in the shock front. A deflagration starts at the hot spot and grows spherically until it begins to interact with the outward growing deflagrations from neighboring hot spots. Behind the deflagration front, the solid explosive crystal has transformed into gas products at high pressure and temperature.

We have used the computer hardware and software at our laboratory to study the details of the deflagration of high pressure and high-temperature explosives, as part of our Grain-Scale Dynamics in Explosives project for the Accelerated Strategic Computing Initiative. In the work reported here, we are using our computer simulations of deflagration to examine the dependence of the calculated deflagration speed on the chemical reaction kinetics and the species energetics.

NUMERICAL METHODS

We report the results of direct numerical simulations of deflagrations at high pressure. The computer simulation program, ALE-3D, which is

under development at this laboratory, includes numerical methods to solve the heat flow equations either explicitly or implicitly. At present, the only solution method available for compressible hydrodynamic flow in the absence of shear strength is explicit. The resulting time step, as determined by the Courant condition for hydrodynamics [3] is larger than the explicit time step for heat transfer [3] for all mesh sizes Δ larger than the critical size Δ_c, where

$$\Delta_c = 2\kappa/c. \qquad (1)$$

Here κ is the thermal diffusivity, and c is the sound speed. Typical values for explosives and explosive products are $\kappa \sim 10^{-7}$ m^2/s, $c \sim 5 \cdot 10^3$ m/s, so that $\Delta_c \sim 0.04$ nm.

In standard solution methods for heat transfer, temperature is defined on the nodes of a finite element mesh. This is not directly compatible with standard solution methods for hydrodynamic flow in which all thermodynamic variables are defined within the volume of the finite element. Although methods have been developed to treat coupled, explicit hydrodynamics and heat transfer on the same mesh [4] the methods were not readily extended to include implicit heat transfer solutions. Instead, Nichols [5] developed a method that forces communication between the node-centered and element-centered temperature fields to have the appropriate time delay. This methodology was used for all the computer simulations reported here.

A challenging part of our numerical simulations is the incorporation of multiple chemical reactions using Arrhenius kinetics. Since the net result of these reactions is typically a 2500 K increase in temperature, the coupled equations become mathematically stiff. Nichols [6] developed a solution method that enforces simultaneous solution of pressure and temperature equilibrium for all species present in a finite element that is consistent with the chemical reaction rates. That method of coupling changes to species concentrations with temperature and hydrodynamics is used in all the simulations reported here.

In all of these simulations, we have ignored the contribution of species diffusion in smearing out the concentration of the intermediate products. The transport properties as calculated by Bastea [7] show that in the pressure range of interest to detonation, between 1 and 50 GPa, the ratio of species to temperature diffusivity changes from the low-pressure, ideal gas value of 1.0 to the high-pressure value of 0.01. We can estimate the effect that change has on the calculated deflagration speed. Zel'dovich and Barenblatt [8] report a simplified set of equations for one-dimensional flame propagation where the ratio of species to thermal diffusivities is a parameter. For that case, the change in ratio from 1 to 0.01 results in a change of calculated flame speed of about a factor of four. From the solution of their equation set, our results will be qualitatively correct, but quantitatively in error. Some quantitative comparisons of our simulations with Diamond Anvil Cell (DAC) experiments in this pressure range have already shown that to be the case [9].

MATERIAL PROPERTIES

The review of Menikoff and Sewell [10] describes some of the properties needed for mesoscale simulations of explosives. They reported mainly the mechanical properties of the unreacted HMX explosive crystal. In addition, we need to describe the chemical reaction rates, and the mechanical, thermal, and transport properties of the various species present. We begin with the simplified global kinetics scheme reported by McGuire and Tarver [11] for HMX. That scheme includes a first, endothermic step, followed by a second, mildly exothermic step to form relatively high-molecular weight gas mixture, and a final exothermic step to form the final products. We identify the product of the first endothermic step as δ-HMX, although the endothermicity of Tarver's reaction scheme is significantly larger than the measured latent heat of the β-δ transition. We assumed that the intermediate gas products of the second step are those identified by Tarver: CHOH, N_2O, HCN, and HNO_2.

We have taken the solid equation of state for the β- and δ-phase HMX to be simple Mie-Gruneissen forms with constant specific heat. The compressibility of HMX is based on Yoo's DAC measurements [12]. We used Bridgman's correlation [13] for high-density fluids to estimate the pressure-dependent thermal conductivity. We constructed complete equation of state tables for the intermediate and final products using CHEQ [14].

Since exponential-6 potential parameters are not available for the intermediate products, they were estimated by Bastea based on results of classical MD simulations performed by Wu [15]. The transport properties for the two gas species are calculated by a method developed by Bastea [7] and incorporated as additional table entries.

SIMULATION GEOMETRY AND BOUNDARY CONDITIONS

The underlying simulation geometry is one-dimensional slab symmetry, which is treated as a stack of cubes in ALE-3D. All four lateral faces are adiabatic symmetry planes. The material occupying the cubes is β-HMX at the desired pressure, $p0$, and at room temperature. The input boundary is held at the constant pressure $p0$, and is given a temperature ramp from room temperature to the approximate flame temperature over a time of five (or sometimes ten) psec. The flame is propagated a distance of approximately one μm, which is about half the initial length of the stack of cubes. At that time, typically 200 nsec, the propagation velocity is observed to be constant. Most of the simulations were performed with a cube dimension of four nm, which results in an average time step of 0.5 psec, for a total of 0.6 M calculational cycles. A few simulations were performed with smaller mesh sizes (2 and 1 nm) to confirm that convergence with zone size had been achieved. The simulations with nominal resolution take 15 to 20 hours each on a 400 MHz SG workstation.

RESULTS AND ANALYSIS

Computer simulations of deflagration for the nominal set of properties are well-represented by the functional form

$$v = Ap^n \qquad (2)$$

where A takes the value 2.6 and n takes the value 0.38 for pressure in GPa and propagation velocity measured in m/s.

We performed variations on the nominal properties to determine the effects of changes in them to the calculated deflagration speed. We altered the heat of formation for the product of the first, endothermic step from its nominal value of 420 J/g relative to the heat of formation of the reactant, β-HMX. For the cases where the heat of formation was taken to be 0 or –420 J/g, the values of the burn rates were identical to within 0.2%, which is the precision that we can extract the flame speed from the simulations. Changing the activation energy of the first reaction to 90% of the nominal value, and changing the frequency factor to 110% of the nominal value similarly had no affect on the calculated flame speed.

Changes to the energy of formation of the intermediate products had a noticeable effect. Increasing (or decreasing) the heat of formation by 420 J/g from the nominal value of -540 J/g relative to β-HMX had the effect of decreasing (or increasing) the burn velocity at all pressures by 10%. The power-law dependence of the flame speed was not changed. Changing the kinetic parameters of the second reaction in a similar way to the way we changed them for the first reaction resulted in no change to the calculated flame speed.

In contrast, the heats of formation of the final product and the kinetic parameters to form the final product have a substantial effect on the calculated burn rate. Reducing the heat of formation of the final product from –6000 J/g relative to β-HMX to –6400 increases the flame speed by 18% at all pressures. Increasing the heat of formation to –5600 J/g reduces the velocity to 85% of the nominal value at all pressures. Reducing the activation energy of the last step by 10% increases the velocity to 145% of nominal at all pressures. Increasing the frequency factor by 10% increases the burn velocity at all pressures to 195% of nominal. We changed the order of the third reaction from second to first order. The pressure dependence of the flame speed changed from n = 0.38 to n = 0.20. Figure 1 shows the effect of changes to the final reaction on the flame speed.

CONCLUSIONS

The results of our simulations show that only those parameters associated with the substantially exothermic step have a significant influence on the propagation speed of high-pressure deflagrations. Reducing the activation energy or increasing the frequency factor of the exothermic reaction makes the temperature gradient steeper, which is associated with faster flame propagation. Decreasing the
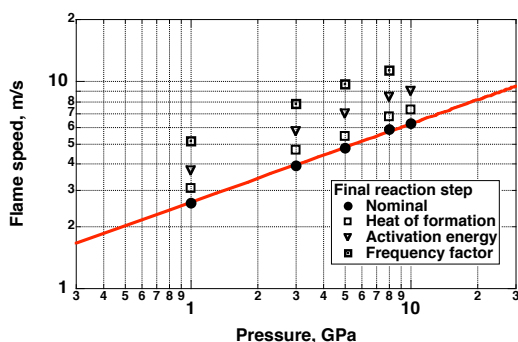
Figure 1. Calculated isobaric flame sped as a function of pressure for various perturbations to the nominal properties of the exothermic reaction step. The activation energy and frequency factor were changed 10%, and the head of formation of the final products was reduced 7%.

heat of formation of the final product results in an increase of the final temperature. At 10 GPa, for example, the flame temperature increases from the nominal value of 2820 to 2960 K. This temperature rise, in turn, affects the kinetic rates as well.

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